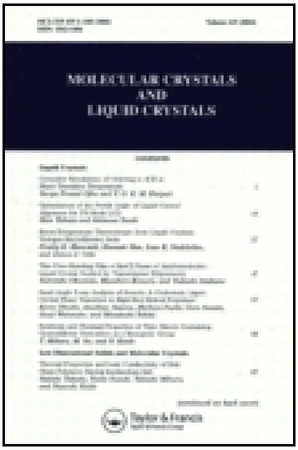

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KC_4, A NEW GRAPHITE INTERCALATION COMPOUND

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Abstract New stage 1 graphite-potassium intercalation compounds have been synthesized. They are very rich in metal, as each intercalated sheet consists of two superimposed potassium planes. The chemical formula is close to KC_4. Five different phases were observed. They were studied by X-Ray diffraction. Electrical measurements were carried out on two phases.

INTRODUCTION

Heavy alkali metal intercalate easily into graphite; the corresponding binary phases have been the most studied Graphite Intercalation Compounds (GICs).

The intercalation of potassium was achieved 65 years ago [1]. The well known compound, whose chemical formula is KC_8, is a first stage phase. It has a bronze colour, with a metallic brightness. Each intercalated sheet is a potassium monolayer with an hexagonal two dimensional structure, epitaxic with the graphene layer. The three dimensional crystal structure of this phase is well known [2].

KC_8 was considered as the saturated binary potassium compound. Some "KC_4" phases were obtained [1,3] by immersing graphite in liquid potassium, but these results were not confirmed [4]. Recently, it was found that, by means of high pressure [5,6], it was possible to synthesize some phases containing a higher alkali metal amount : KC_6, KC_4. In these compounds, the intercalated sheets are also potassium monolayers but their compactness is much higher than in KC_8. However, these phases are not stable at ambient temperature when the pressure is released : they lead to a mixture of free potassium and KC_8.

Independently, some ternary compounds exhibit also an atomic C/K ratio of 4 [7,8]. In such compounds, like $KH_{0.8}C_4$ or $KHgC_4$, the intercalated sheet is three-layered : two potassium layers, which have a density close to that of KC_8, are superimposed, surrounding the plane constituted by the third element. Theoretically, the elimination of the central layer would give a binary phase with the chemical formula KC_4. It seems in fact quite impossible as the central layer certainly ensures the stability of the intercalated sheet[9]. However, in these ternary compounds, the central layer is constituted by weakly electropositive atoms (M = Hg, Tl, Bi, Sb, As), and the M/K ratio is always high (it is comprised between 0.5 and 1.5). By replacing the atoms of the central layer with a very strongly electronegative element as oxygen, we thought that a very small O/K ratio will be sufficient to allow the superimposition of two potassium layers in each graphitic interlayer space.

In this paper, we describe new "pseudo binary" compounds with double layers of intercalated potassium, prepared with potassium containing some "impurities" of oxygen.

EXPERIMENTAL RESULTS

The samples are prepared from HOPG platelets or single crystals. The reaction between slightly oxidized liquid potassium or better, mixture of pure potassium and KO_2 (1% at. oxygen), and the graphite sample is carried out in a stainless steel reactor, under an argon atmosphere. The reaction temperatures vary from 300°C to 600°C, and the reaction times were comprised between a few hours and four days.

Five first stage phases have been obtained. They can be distinguished by their interplanar distances, and they are identified using a greek letter :

α-phase : $d_i = 840$ pm β-phase : $d_i = 850$ pm γ-phase : $d_i = 860$ pm
δ-phase : $d_i = 870$ pm ε-phase : $d_i = 890$ pm.

The β-phase has been isolated at various times (reaction temperature : 370°C, reaction time : 48 h.). The δ- and γ-phases were also obtained quasi pure. So far the two other phases could not be isolated. The five phases exhibit a purple colour. They are much more air and water stable than KC_8. The chemical analysis gives the formula $KC_{3.8}$, identical to that previously mentioned[3] (close to KC_4), with perhaps a small amount of oxygen.

When the β-phase is heated under vacuum in a sealed pyrex tube, it begins to decompose around 230°C giving the classical binary compound KC_8 (potassium monolayers). Nevertheless, at 280°C, a second phase appears, corresponding to a blue second stage compound with double layers of potassium, whose chemical formula is also KC_8. Dilatometric measurements on the pure phases or on mixtures of phases always gave values around 150%, in good agreement with the theoretical values, calculated from the crystallographic data.

Figure 1 shows the *00l* X-Ray diffraction pattern of the pure β-phase : the 003 reflexion is the most intense, the 005 reflexion does not appear; it is interesting to note that the ratio of the *00l* reflexion intensities is approximately the same for the five compounds. We suppose that the structure along the c-axis is quite similar for all phases.

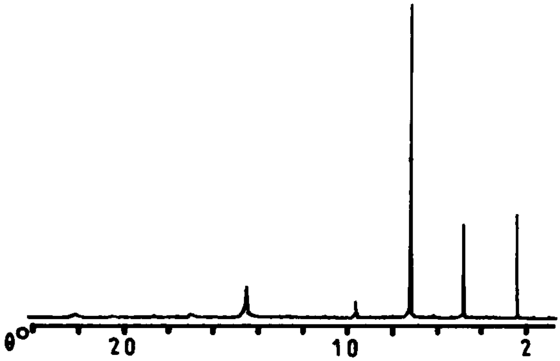


FIGURE 1 *00l* diffraction pattern of β-compound (Mo $K\alpha_1$ radiation).

The Fourier transform of the *00l* structure factors allows to display the electronic density profile along the c-axis. Figure 2 shows both experimental and calculated electronic density profiles (in good agreement) corresponding to the β-phase. Two layers of potassium appear clearly in the interlayer space. The distance between these two planes reaches 298 pm and each potassium plane is at 276 pm from the nearest graphene layer (268 pm only in KC_8).

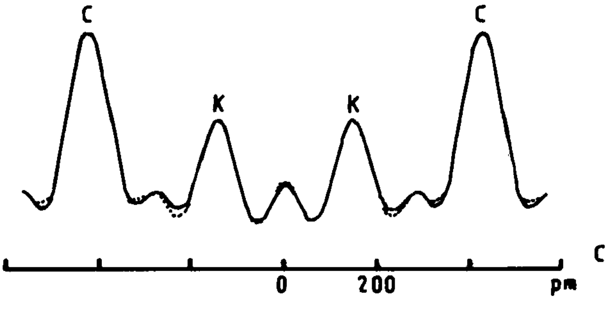


FIGURE 2 Electronic density profile along the c-axis of β-compound (solid line : calculated; dashed line : experimental).

The *hk0* X-Ray diffraction patterns have been registered for several phases, from both HOPG and graphite single crystal samples. A preliminary study shows that the intercalated bilayered sheets are highly organized. Their two dimensional arrangement are complex, and very different from that of KC_8; the in-plane structure seems to be different for each compound. Moreover the expansion of the in-plane carbon-carbon distances is particularly large. It is close to 1.1% for the β- and δ-phases, whereas the value is 0.8% for KC_8. Figure 3 shows the 100 and 110 reflexions in δ- and KC_8 phases compared with pristine graphite. In such compounds, the charge transfer to the graphene layers seems to be particularly high.

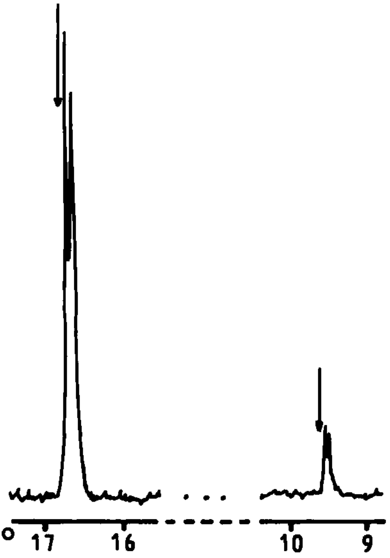
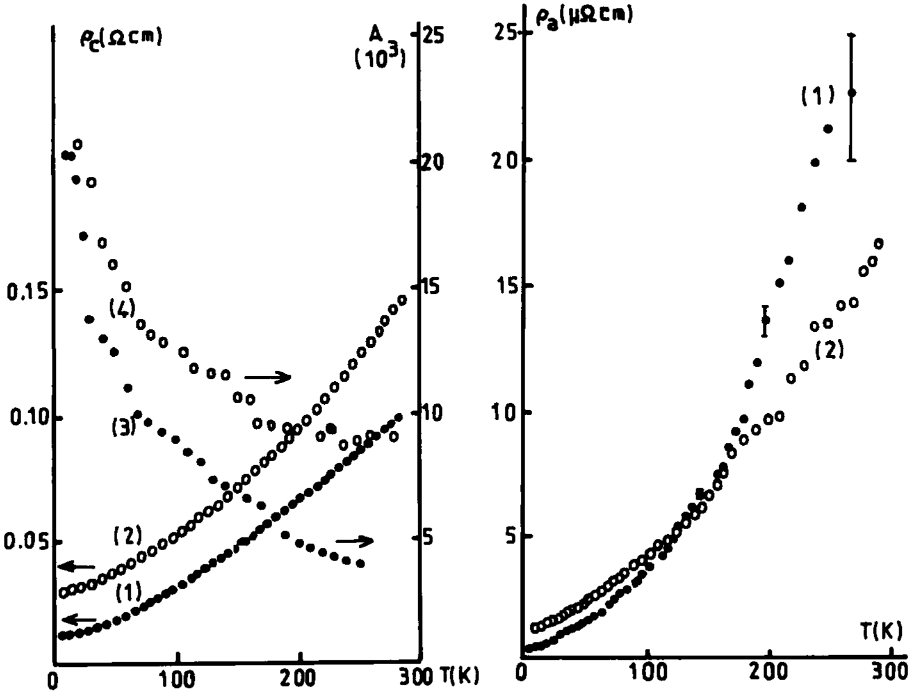


FIGURE 3 100 and 110 reflexions of graphene planes in δ- and KC_8 phases (arrows show the positions of these reflexions in pristine graphite) (Mo $K\alpha_1$ radiation).

The basal plane and c-axis resistivity, ρ_a and ρ_c respectively, were determined between 290 K and 4.2 K for β- and γ-phases. Figure 4 and table I illustrates these results.

TABLE I Electrical resistivity at 270 K and 10 K for β- and γ- phases.

	270 K			10 K		
	ρ_a (μΩcm)	ρ_c (Ωcm)	ρ_c/ρ_a	ρ_a (μΩcm)	ρ_c (Ωcm)	ρ_c/ρ_a
β	14.1	0.134	9500	1.2	0.0302	25200
γ	22.5	0.092	4100	0.5	0.0117	23500



4a

4b

FIGURE 4 4a c-axis resistivity versus temperature for γ-phase (1) and β-phase (2)
Anisotropy ρ_c/ρ_a for γ-phase (3) and β-phase (4)
4b Basal plane resistivity vs temperature for γ-phase (1) and β-phase (2)

The basal plane resistivity is quite higher than in the KC_8 compounds. The β- and γ-phases are very similar with regards to chemical composition, and in fact the differences of in-plane resistivity could be due to a higher level of defects in the γ-phase, arising from synthesis at a higher temperature. The residual resistivity ratio, between 10 and 40, is much lower than that of the KC_8 binary compounds. As far as c-axis conductivity is concerned, most models involve a strong influence of the c-axis repeat distance. The γ-phase has the higher c-axis distance, but it has the lowest room temperature c-axis resistivity. This is a further indication for an increased level of defects in the γ-phase. Room temperature anisotropy lies between 4000 and 10,000, rising to 25,000 at low temperature. In the GICs family such conductivity anisotropy is not very high compared to that of acceptor compounds, often around 10^6, but much higher than that of the MC_6 or MC_8 binaries, which are often considered as three dimensional compounds with their anisotropies in the 10 - 100 range at room temperature.

DISCUSSION AND CONCLUSIONS

The existence of five different phases raises a question about the origin of the various intercalated sheets. Several kinds of intercalated sheets have also been observed in the graphite donor-type compounds with metallic alloys and hydrides. Their thickness and structure are different, and their chemical composition too. The observation of various phases of two-layered potassium graphite compounds is relative to a general phenomenon which also appears here, where the third element is present in a very small quantity. Thus, the existence of several kinds of intercalated sheets could be explained by the instability of a single phase during the cooling from reaction temperature to room temperature. Stable at the synthesis temperature, it segregates into different phases[10] which are probably metastable. Consequently, we think that the chemical formulas of the five phases are probably roughly the same, with perhaps small differences in the oxygen amount. This could also explain the weak differences between the observed interplanar distances as well as strong disparities in the two dimensional structural arrangement. The impossibility of isolating some of the phases is also a consequence of this dismutation phenomenon.

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